Interactions Among Chemical Speciation, Algal Accumulation, and Biogeochemical Cycling of Toxic Metals in a Major U.S. Naval Harbor (Elizabeth River, VA)

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LONG TERM GOALS

Our long-term research goal is to determine the mechanisms and factors that regulate the uptake and accumulation of pollutant metals by phytoplankton and other particles in estuaries and the effect of this accumulation on the removal and biogeochemical cycling of metals.

OBJECTIVES

Study the influence of metal speciation and metal/metal interactions on the particulate cycling and removal of pollutant metals (Zn and Cd) in the Elizabeth River/Hampton Roads Estuary, home of the US Navy Atlantic Fleet. We are especially interested in the role of metal uptake by plankton as well as in our ability of to predict removal of metals from algal uptake models. These models will be based on field data for free ion concentrations of controlling metals (Zn, Cd, Cu, and Mn) and laboratory data on algal uptake as functions of free ionic concentrations of these metals.

APPROACH

In collaboration with John Donat and Dave Burdige at Old Dominion University, we are conducting an integrated field study of the chemistry and biogeochemical cycling of pollutant metals in the Elizabeth River and adjacent waters. We collected near-surface (1 m) water samples along a six-station transect from highly metal-polluted waters of the Elizabeth River to the less contaminated waters of the lower Chesapeake Bay. This transect was sampled during late July, 1999 and again during May, 2000. The samples were analyzed by Donat for total and dissolved concentrations of Cu, Cd, Zn, and Mn; free ion concentrations of Cu, Cd, and Zn; and concentrations and binding strengths of chelators that complex these metals. We (Sunda and Huntsman) measured size fractionated Chl *a*.

We (Sunda and Huntsman) conducted radiotracer experiments in aliquots of the surface samples to determine *in situ* rates of particulate and algal uptake of Cd and Zn and photosynthetic CO_2 fixation. Specific rates of uptake of Cd and Zn and of C-fixation were determined by addition of radiotracers (^{109}Cd, ^{65}Zn and ^{14}C-bicarbonate). Subsamples were amended with the strong chelator DTPA and a mild reductant (ascorbate) to help differentiate radio-labeled metals adsorbed to particles or associated with Mn oxides from those accumulated within plankton.

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WORK COMPLETED

In the past year, we continued our computational analysis of results from our July, 1999 field study. We also completed a second field trip to the Elizabeth River estuary in May. Results from our July study were presented at two international meetings: ASLO 2000, held in Copenhagen, Denmark in June and a symposium on "Trace metal speciation in aquatic systems", held in Porto, Portugal in August.

RESULTS

Chlorophyll *a* and ^{14}C-fixation showed a 3 to 5-fold range for the six stations sampled in May, 2000 (Table 1), somewhat less than the 10-fold range observed in July, 1999. The highest values in May occurred at the mid-estuarine stations 4-6.

Results of the radiotracer addition experiments in May were qualitatively similar to those for July. As before, a much greater fraction of ^{65}Zn than ^{109}Cd was associated with particles. Each radionuclide showed rapid particulate accumulation within the first hour, followed by a much more gradual uptake that was nearly linear with time over the next 4 to 7 hours. The time-course data for the fraction of particulate radionuclide vs time was fit to a first order reaction rate model:

$$-d[^{65}Zn]/dt = k[^{65}Zn] \quad or \quad -d[^{109}Cd]/dt = k[^{109}Cd]$$

$[^{65}Zn]$ and $[^{109}Cd]$ are the fractions of the radionuclides remaining in solution. The first order rate constant *k* gives the specific rate of particulate metal uptake. Integration of the above equation gives:

$$\ln[^{65}Zn] = -k\,t + \ln[^{65}Zn]_{t=0} \quad or \quad \ln[^{109}Cd] = -k\,t + \ln[[^{109}Cd]_{t=0}$$

Regressions of $\ln[^{65}Zn]$ or $\ln[^{109}Cd]$ vs time fit the first order model for time period of 1 to 8 h. These regressions all show a negative y-intercept reflecting the initial rapid loss of dissolved radiotracer due to adsorption onto particles. The negative slope of these regressions gives the specific rate of the slower particulate uptake process while the y-axis intercepts can be used to estimate the rapid adsorption of the metals onto surfaces. Both sets of values are given in Table 1.

Table 1. Long-term particulate accumulation rates and rapid surface adsorption values for ^{65}Zn and ^{109}Cd in one-meter samples collected at stations in the lower Chesapeake Bay (St. 3 and 4), Hampton Roads (St. 5), the Elizabeth River (St. 6-8). Measurements made in May 2000.

Station	Salinity	pH	Chl a (nmol/l)	^{14}C Fixation (μmol/l/h)	Part. ^{65}Zn Uptake Rate (% h^{-1})	^{65}Zn Adsorp. (%)	Part. ^{109}Cd Uptake Rate (% h^{-1})	^{109}Cd Adsorp. (%)
3	22.1	8.12	3.49	1.7	1.41	6.32	0.108	0.40
4	19.5	8.11	10.96	5.4	3.0	9.11	0.245	0.77
5	17.3	8.01	11.23	7.0	3.62	14.8	0.241	1.09
6	17.1	7.74	10.7	8.5	2.45	6.32	0.254	0.92
7	16.8	7.53	8.72	5.7	1.08	4.14	0.103	0.60
8	16.0	7.41	4.24	2.8	0.47	3.05	0.060	0.36

The specific rates determined from the above analysis ranged from 0.47 to 3.6 % h^{-1} for Zn and 0.06 to

0.25 % h^{-1} for Cd, indicating much higher rates for particlate Zn formation (Table 1). Estimates of rapidly adsorbed radionuclide were 3.0 to 15% for Zn and 0.40 to 1.09% for Cd, again showing much higher values for Zn (Table 1). There was a general correlation among specific particulate uptake rates for Zn and Cd, initial adsorption values, Chl *a* and ^{14}C-fixation rates, suggesting that all of these parameters are linked. Highest values for metal adsorption and long term particulate uptake were all found in the broad Chl *a* maximum at stations 4-6 in Hampton Roads and the lower Elizabeth River. The correlation between specific rates of long-term particulate Zn and Cd formation and Chl *a* suggests that these rates reflect cellular uptake of Zn by algae and other plankton. This hypothesis is also supported by a strong suppression of long-term particulate Zn and Cd uptake with the addition of azide, a biological poison, observed in both the July and May radiotracer experiments.

In the time course experiments, the radiotracer metals taken up onto particles over 5-8 hours were subjected to two separate washes: 1 mM DTPA, a strong chelator that desorbs metals from surfaces; and 1 mM ascorbate at ambient seawater pH, a mild reducing agent that reductively dissolves Mn oxides. The DTPA wash removed 34-58% of the particulate ^{65}Zn and 21-55% of the particulate ^{109}Cd, confirming that adsorption is an important mechanism for particulate metal association. Ascorbate removed 5-20% of the particulate ^{65}Zn and 10-34% of the ^{109}Cd, with highest values occurring in the three Elizabeth River stations (stations 6-8), where Mn concentrations are highest. These results suggest that most of the Cd and ~ a third of the zinc adsorbed to particles in the Elizabeth River is associated with Mn oxides, which are known to be strong adsorbers of heavy metal ions.

In the past year, we continued our analysis of results from the July, 1999 field study by combining our radiotracer rate measurements with John Donat's measurements of dissolved and free ion concentrations of Zn, Cd, and Mn (Tables 2&3). By multiplying specific rates of Zn and Cd particulate uptake by dissolved concentrations of the metals we were able to compute particulate Zn and Cd uptake rates in units of mol/l/h. These rates were then divided by carbon fixation rates to yield the Zn:C and Cd:C assimilation ratios for the field plankton communities (Tables 2&3). In July, the dissolved zinc concentrations decreased by 30-fold and free zinc ion concentrations by 3000-fold between the most upstream station (St. 8) and station 5 at the mouth of the Elizabeth River. The large decreases apparently are due to uptake of Zn by phytoplankton within the large algal bloom in the lower Elizabeth River. Our field Zn:C plankton values increased by 11-fold with increasing log [Zn^{2+}] in the estuarine water (Fig. 1). A plot of the field Zn:C plankton values vs log [Zn^{2+}] is similar to curves for cellular Zn:C vs log [Zn^{2+}] measured in the algal cultures grown in metal ion buffer

Table 2. Dissolved Zn, [Zn^{2+}], specific and absolute rates of particulate zinc uptake, C-fixation rates, and computed Zn:C particulate assimilation ratios for the July, 1999 sampling trip.

Station	Diss. Zn (nM)	Log [Zn^{2+}]	Zn uptake rate (%/h)	Zn uptake rate(nmol/l/h)	C-fixation rate (µmol/l/h)	Zn:C ratio (µmol/mol)
3	8.2	–11.07	1.54	0.126	4.87	25.9
4	4.7	–10.79	3.11	0.146	8.43	17.4
5	3.7	–11.22	2.19	0.081	9.4	8.6
6	27	–9.22	14.15	3.9	55.9	69.8
7	52.3	–8.02	5.51	2.9	38.7	75.2
8	89.1	–7.64	3.85	3.4	36.0	95.3

Table 3. Dissolved Cd, [Cd^{2+}], [Mn^{2+}], specific and absolute rates of particulate Cd uptake, field Cd:C particulate assimilation ratios, and modeled Cd:C for a coastal diatom for the July, 1999 sampling trip.

Station	Diss. Cd (nM)	Log [Cd^{2+}]	Log[Mn^{2+}]	Cd uptake rate (%/h)	Cd uptake rate (pmol/l/h)	Measured Cd:C ratio (µmol/mol)	Modeled Cd:C ratio (µmol/mol)
3	0.098	–11.81	-8.25	0.24	0.235	0.048	0.068
4	0.137	–11.51	-7.88	0.34	0.466	0.055	0.082
5	0.148	–11.38	-7.52	0.20	0.296	0.031	0.051
6	0.248	–11.13	-6.71	0.46	1.14	0.020	0.0139
7	0.277	–11.03	-6.32	0.45	1.25	0.032	0.0083
8	0.338	–10.86	-6.11	0.23	0.777	0.021	0.0080

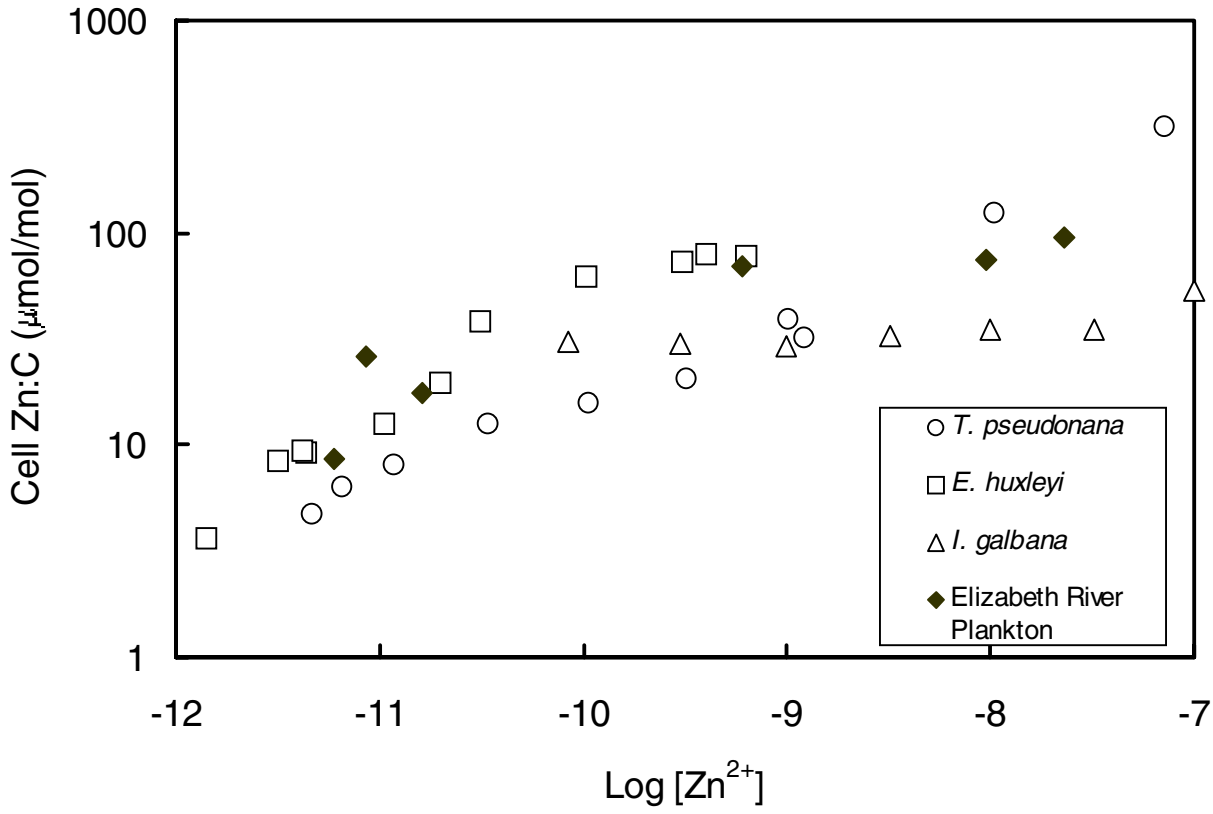

Figure 1. Relationship between Zn:C and log [Zn^{2+}] for natural plankton in the Elizabeth River/Hampton Roads system and algal species grown in metal ion buffer systems: **Thalassiosira pseudonana, Emiliania huxleyi,** ***and*** **Isochrysis galbana**.

systems. The field/lab agreement again supports the hypothesis that the long term particulate uptake of Zn results from accumulation by phytoplankton. It provides a field confirmation of our central hypothesis that the uptake of metals by phytoplankton is controlled by the free metal ion concentration.

In July, there was only a 2.3-fold decrease in dissolved Cd and 3.3-fold decrease in [Cd^{2+}] between station 8 and station 5, sharply contrasting the 30-fold decrease in dissolved Zn and 3000-fold decreased in [Zn^{2+}] observed at these stations. The much smaller decrease in Cd values is consistent with the much lower specific rates of particulate Cd uptake observed in our radiotracer studies (Tables 2&3). Also in contrast to Zn, the particulate Cd:C assimilation ratios decreased with increasing [Cd^{2+}]. These paradoxical results may be explained by the antagonistic interactions between Cd^{2+} and Mn^{2+} in phytoplankton due to uptake of Cd by the cell's Mn transport system (Sunda and Huntsman 1996, 1998, in press). As a result of these interactions, Cd:C values in the coastal diatom *Thalassiosira pseudonana* were found to be proportional to [Cd^{2+}], but inversely proportional to [Mn^{2+}]. Between station 8 in the Elizabeth River and station 3 in the Chesapeake Bay, [Cd^{2+}] decreased by 9-fold, while [Mn^{2+}] decreased by 138-fold (from 776 to 6 nM). From our measured values for [Cd^{2+}], [Mn^{2+}], and [Zn^{2+}] at our six field stations and previous data for uptake of Cd by *T. pseudonana* as functions of these controlling parameters (Sunda and Huntsman 1996), we were able to compute Cd:C for diatoms growing in the estuarine waters. These modeled values agree reasonably well with the field particulate Cd:C assimilation ratios, especially for stations 3-6 where eucaryotic algae were the main phototrophs (Table 3). The agreement between the field Cd:C particulate estimates and the modeled diatom Cd:C values suggest that phytoplankton are largely responsible for the observed long term particulate uptake of Cd. Furthermore, an antagonism between Cd and Mn, coupled with the large increase in [Mn^{2+}] can readily explain the low particulate Cd uptake and Cd:C assimilation values in the Elizabeth River despite higher Cd ion concentrations. This suppression algal uptake of Cd by Mn appears to be responsible for the low estuarine removal of dissolved Cd.

IMPACT

Our results indicate that the pollutant metal Zn strongly adsorbs onto particles and is taken up by phytoplankton, which removes it from solution and transports it to the bottom. This removal has a major impact on the concentration and cycling of Zn in eutrophic estuaries such as the Elizabeth River. The decrease in concentrations decreases Zn toxicity, while the removal to the bottom leads to Zn accumulation in harbor sediments. By contrast, Cd shows a much lower uptake by plankton and other particles. Consequently, algal growth should have a lesser impact on Cd concentrations, toxicity, and transport to the sediments. This work indicates fundamental links among anthropogenic nutrient inputs, algal blooms, and the concentrations, toxicity, and fate of pollutant metals in harbor systems.

RELATED PROJECTS

As pointed out above, this work is being conducted in close collaboration with the ONR Harbor Processes project of John Donat and Dave Burdige at Old Dominion University.

TRANSITIONS

The results of this collaborative project will be used to construct more realistic conceptual and numerical models of pollutant metal cycling, fate, and biological effects in harbors and related estuarine systems.

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